ADSORPTION STUDIES OF MALACHITE GREEN USING ACTIVATED CARBON PREPARED FROM JACKFRUIT SEEDS

A Thesis submitted in partial fulfillment for the award of the degree of

Bachelor of Technology in Chemical Engineering

BY

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CERTIFICATE

This is to certify that the thesis entitled, **"ADSORPTION STUDIES OF MALACHITE GREEN USING ACTIVATED CARBON PREPARED FROM JACKFRUIT SEEDS**" submitted by Mr Ranjit Behera in partial fulfillment for the requirements for the grant of Bachelor of Technology Degree in Chemical Engineering at National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by him under my supervision and direction.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

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ABSTRACT

This project work focuses on study of adsorption of Malachite Green dye on jackfruit seed carbon. Inexpensive and environment friendly adsorbent is used for the removal of malachite green dye from aqueous solution. Studies were conducted to check the effect of different experimental parameters such as adsorbate dose, temperature, and initial concentration of malachite green, contact time, pH. The optimum conditions were evaluated from these parameters. The optimum conditions include contact time of 60 minutes, pH 5, temperature 30^{o}C and 1gm adsorbate dosage. Study of adsorption isotherms was carried out at this optimum condition which gives us the best fitting adsorption isotherm model. The equilibrium data was fitted to Langmuir and Freundlich models and the results showed that the adsorption data agreed well to Freundlich isotherm than Langmuir isotherm. The results indicated that jackfruit seeds carbon can be used as an alternative adsorbent for treatment of effluents containing malachite green dye.

Keywords- adsorption, dye, jackfruit seeds, isotherm, activated carbon

Chapter 1

Introduction

1. INTRODUCTION

1.1 Dyes

Dyes are coloured substances which has the tendency to get attached to the substance on which it is being used. For most of the cases, dyes are applied in the form of aqueous solutions. External substances called mordent are used for better execution of dye on the fiber. Both pigments and dyes absorb some wavelengths of light more than others.Hence they appear coloured. There are many reasons for which dye possess colour; the basic reason being that it absorbs light in the visible spectrum (400–700 nm). Another reason is that they contain some colour-bearing groups called *chromophores*. The structure of dyes shows double and single bonds alternatively which is the last reason for which dyes shows resonance property which stabilizes the organic compounds. When any of these properties are not present satisfactorily, the chemical substance loses its colour. Dyes contain another substance called auxochromes which are also known as colour helpers. Examples of auxochromes includes Carboxylic acid, Sulfonic acid, Amino and Hydroxyl groups. Auxochromes are used to change the dye solubility but they are not sensible for colour of the colourant. There are other coloured substance called pigments but are different from dyes in the way that they are hardly soluble and has no inclination to attach to. Dyes can be classified into naturally occurring or synthetic/artificial. The colourants which are acquired from naturally occurring substances such as plants and mineals are called Natural dyes. Most of naturally occurring dyes are acquired from plant sources like leaves, wood, bark and roots of trees. Increased demand for cheap, easily available and simply applied dyes led to the invention and rapid growth of synthetic dyes.The presence of dye and its conducive compounds have always been unwanted in water for use in either factories or for household purposes. Color may be an obvious waste item. Different types of coloring materials like dyes, inorganic pigments, tanning, lignin etc. all grant colour. Amongst the complicated industrialized effluent with different sorts of coloring materials, dye wastes are major constituent. Currently, there are more than eight thousand different sorts of dyes in market having various chemical properties. The pharmaceutical industries, dye and dye intermediates industries, Kraft bleaching, paper and pulp industries are some of the industries using dyes. Other industries include fabric industries, tannery, cosmetics, rubber ,paper etc. Dye intermediates and organic colorants are responsible for colour of a dye. Discolouration of industrial waste is one of the foremost and the toughest challenge faced by the textile, pulp and paper industries, dye producing, attributable to toxics nature of dyes. Based on the ions present in it, dyes are mainly classified in 3 categories: (i) Basic dyes (cationic in nature) (ii) direct, acid and reactive dyes (anionic in nature), and (iii) dispersed dyes (nonionic in nature).

1.2 Harmful Effects of Dyes

All the dye wastes, produced from diferent sorts of commercial enterprises have harmful impacts on microbial inhabitants and may be toxic and even deadly to mammals. These dyes have the potential to cause diseases such as allergic eczema, skin irritation problem, mutations and cancer. The few chemicals used to create dye are very harmful, cancer-causing agents and hormonal disrupter. The excessive utilization of dyes causes problems in the environment. This prevents sunrays infiltration into the water and declines photosynthetic activity which additionally brings about problems in the atmosphere.

Malachite green is hazardous dyes which not just have lethal properties influencing the cells of mammals but is also a significant reason for making tumor in liver. The dye released in water bodies without being dealt with appropriately, affects the life-cycle of amphibian creatures and plants by hindering the infiltration of sunlight. They cause depletion of dissolved oxygen due to conjointly increase in the biological oxygen demand (BOD) to sustain marine life. As few dyes are horrendously cyanogenics, they cause damage directly or inhibit their chemical action abilities. At low concentrations, dyes cause adverse effect on the marine life and therefore, the food cycle. Dyes have molecules in equilibrium, created to fight against the degradation by sunlight, biological, chemical and many other areas.

Approximately a million metric tons of dyes are produced annually in the era of azo dyes (R1-N=N-R2), which imply about 72% of the total dyes. About 60,000 metric tons of dyes are being made in India, which is roughly $1/20^{th}$ of total world production. According to the recent survey, about two third of its market are being utilized in textile industries. It has been demonstrated that 14% of the artificial textile dyes utilized consistently are released to water streams. Waste water treatment plants are the real wellsprings of these to the environment. Because of the obstinate and complex nature in structure of dyes, it is extremely hard to decolorize dyes, which make it mandatory to dispose them from waste stream before being tossed out into the main stream. The gushing from a dye house normally has 0.5–0.7 g dye.

1.3 Removal methods of Dyes

Process	Technology	Advantages	Disadvantages
Conventional treatment processes	Coagulation Flocculation Biodegradation	Simple, economically feasible	High sludge production, handling and disposal problems
		Economically attractive publicly acceptable treatment	Slow process, necessary to create an optimal favourable environment, maintenance and nutrition requirements
	Adsorption on activated carbons	The most effective adsorbent, great, capacity, produce a high-quality treated effluent	Ineffective against disperse and vat dyes, the regeneration is expensive and results in loss of the adsorbent, non-destructive process
Established recovery processes	Membrane separations	Removes all dye types, produce a high-quality treated effluent	High pressures, expensive, incapable of treating large volumes
	Ion-exchange	No loss of sorbent on regeneration, effective	Economic constraints, not effective for disperse dyes
	Oxidation	Rapid and efficient process	High energy cost, chemicals required
Emerging removal processes	Advanced oxidation process	No sludge production, little or no consumption of chemicals, efficiency for recalcitrant dyes	Economically unfeasible, formation of by-products, technical constraints
	Selective	Economically attractive, regeneration is not necessary, high selectivity	Requires chemical modification, non-destructive process
	bioadsorbents Biomass	Low operating cost, good efficiency and selectivity, no toxic effect on micro-organisms	Slow process, performance depends on some external factors (pH and salts)

Most industrial systems use activated carbon as an adsorbent for removal of dyes in sewage due to its remarkable adsorption capability. Because of the high price of activated carbon, adsorption is favoured by utilising cheaper materials. Previously conducted research shows that many cheap materials can be successfully used to remove dyes from aqueous solutions. However, very few of them can be used to separate dye successfully from the waste stream. This project attempts to check the potential of jackfruit seeds which is accessible in abundance in India to treat the industrial effluent containg malachite green dye.

1.4 Objective

- To study effectiveness of removal of malachite green using activated carbon prepared from jackfruit seeds and its potential for commercial use.
- To study the effect of different experimental parameters on the adsorption process and to study different models of adsorption isotherms of the process.

1.5 Scope

Study of effects of experimental parameters on adsorption like

- Effect of contact time
- Effect of temperature
- Effect of pH
- Effect of adsorbent dose
- Effect of initial concentration of methylene blue
- Study of the adsorption isotherms

1.6 Problem Statement

Lately, there has been always an interest for activated carbon; henceforth it is a matter of enthusiasm among the researchers to discover a better substitute or a superior source for the creation of cheap and effective activated carbon. Jackfruit seeds does not have much use in domestic or industrial usage, and hence it is regarded a waste. It does have the potential for becoming an effective adsorbent.

Chapter 2

Literature Review

2.1 Activated carbon

It is a great adsorbing material and is used depending on the needs. It is utilised in various industries and has numerous applications e.g. to treat waste water from industries, discolor sugar, medicine. What makes Activated carbon a fine adsorbent is its porous structure which is responsible for the high surface area; 1kg of activated carbon can have approx.4000 square meters of surface area.

Size of the pores determines the type of usage the activated carbon is most suited for. Anything which has a carbon content can be made to activated carbon, and depending on diverse aspects such as economy and attributes of the material it might be suitable or not for production of activated carbon. Two methods are used for the process of preparing activated carbon. *i)physical* and *ii)chemical* .When activating chemically, carbonization and activation happens simultaneously. For carbonization the carbonaceous material is heated without oxygen, also known as pyrolysis. During this process most of the hydrogen ,oxygen and other volatiles are eliminated, leaving the carbon groups structured so that pores are formed which gives adsorbing power to the carbon. After the raw material is carbonized it needs to be activated, when activated the pore structure is enhanced which increases the adsorbing qualities further by extending the pores and burning off tars. A brief description of physical and chemical activation follows. (Bansal et al 1988)

2.1.1 Physical Activation

Physical activation involves two basic steps for activation. The first step involves heat treatment in an inert environment also called *pyrolysis*. Pyrolysis is done around a temperature of 1100^{0}C. During pyrolyis the volatile matter escape from the material and carbon remains which is mostly in the form of char, with an initial carbonaceous structure. Second step involves activation where streams of carbon dioxide gas and steam oxidizes with the carbon treating the char and results in creating pores in material.

2.1.2 Chemical Activation

If raw material is agricultural residue it is better to try chemical activation. Impregnation of raw material is done with activating reagent, that to degradation of the cellulosic material. With this, the precursor is enabled to carbonize even at lower temperature. Chemical activation is used more than the physical activation due to low required temperature and takes shorter duration to activate the material. When the impregnation is done, the material is then heated between 400-800^{o}C at inert conditions. After the activation the material is cooled, washed and dried. The activating agents which are commonly used include phosphoric acid, sulfuric acid and zinc chloride. The pore size in the carbon is set by the impregnation ratio; the bigger the impregnation ratio the bigger the pore diameter. The characteristics of the activated carbon obtained vary with impregnation ratio, activation temperature and composition of the gas used for heating.

Advantages of Chemical activation over Physical activation

• It gives a more porous structure most of the time
• Gives a higher yield
• Needs lower activation temperature

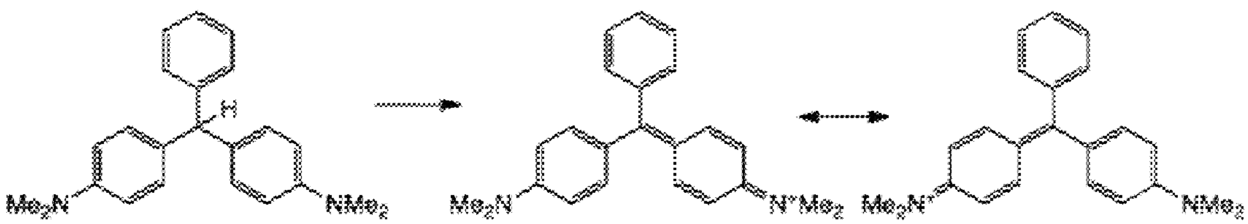
The impregnation gives a few disadvantages, such as:

• Increase in the cost of reactant
• Environmentally harmful properties of the reactant
• Need of washing off the reactant

2.2 Adsorbate

The adsorbate utilized, Malachite green is a natural aggravate that is utilized as a part of different commercial enterprises as dyestuff. It is being used as a colouring material for paper, leather and silk since long. This compound has no connection with mineral malachite. Due to the similarity of colour between them, it is known as malachite green. In industries which uses dyestuffs and pigments, it is used as a triarylmethane dye. In actual form, Malachite green denotes to chloride salt $[C_6H_5C\ (C_6H_4N\ (CH_3)_2)_2]\ Cl$, whereas the term Malachite green only denotes to the coloured cation. In the project, malachite green in the form of oxalate salt is used. The color of the compound is not influenced by the oxalate and the anions. Actually the intense green color of the cation is simply because of its absorption band which lies in the green region. Malachite green color is essentially a cationic dye. Malachite green in diluted form is commonly used in medicine as a local antiseptic. It is effective against parasites, fungal infections and gram-positive bacteria. Malachite Green is prepare by a two step process. First, leuco malachite green LMG is made by the condensation of Benzaldehyde and dimethyl amine. Secondly, by the oxidation of this colorless leuco compound into the cation, malachite green compound is formed.

$$C_6H_5CHO + 2C_6H_5N(CH_3)_2 \rightarrow C_6H_5CH(C_6H_4N(CH_3)_2)_2 + H_2O$$



$$C_6H_5CH(C_6H_4N(CH_3)_2)_2 + HCl + 1/2O_2 \rightarrow [C_6H_5C(C_6H_4N(CH_3)_2)_2]Cl + H_2O$$

Adsorption using activated carbon has been studied for equilibrium isotherm analysis and the kinetic study for the removal of malachite green dye from aqueous solutions . Adsorption studies were accomplished to find the impact of various parameters on dye removal. The parameters include contact time, pH, adsorbent dosage and the initial concentration of malachite green. The removal of dye was found to enhance with increasing contact time till equilibrium was reached.

2.3.Adsorption Isotherms

Adsorption isotherm is generally used to explain adsorption i.e. adsorbate amount on adsorbent as function of concentration (for liquids) or pressure (for gases) at constant temperature. Langmuir and Freundlich isotherms are used to describe the adsorption data.

2.3.1 Freundlich isotherm:

It is an empirical relationship which relates the conc. of a solute upon the surface of the adsorbent with the conc. of solute present in the liquid which are in contact. This model assumes that adsorption occurs on heterogeneous surface.

The linear form can be written as:

$$\ln q_e = lnk_f + \frac{1}{n * lnC_e}$$

Where, k_f and n (dimensionless constants) are Freundlich adsorption isotherm constants, k_f gives adsorption capacity and n gives the adsorption intensity.

2.3.2 Langmuir isotherm:

It gives the relation between the adsorption of the molecules on solid surface to the gas pressure or conc. of a medium above surface of solid at constant temperature. It is based upon the assumption that adsorption process occurs in monolayers.

The linear form of Langmuir expression:

$$\frac{1}{q_e} = \frac{1}{b * q_0 * C_e} + \frac{1}{q_0}$$

Where, C_e = equilibrium conc. of dye solution (in mg/L),

q_e = equilibrium capacity of the dye on adsorbent (in mg/g),

q_o = monolayer adsorption capacity of adsorbent (in mg /g),

b = Langmuir adsorption constant (in L/mg) and has realtion with the free energy of adsorption.

In 2004, A.Mittal, L.Krishnan, V.K.Gupta tried removing the MG using de-oiled soya which is agricultural waste. At low concentrations the removal percentage was nearly 100% whereas in higher concentrations the removal percentage was a bit lower and adsorption occur due to particle diffusion. De-oiled soya was found to be quite effective and is much more economic than the available commercial activated carbon.

In 2006, Z.Bekci, C.Ozveri, Y.Seki, K.Yurdakoc did sorption of malachite green on chitosan bead. The sorption data was found to be following Langmuir isotherm than Freundlich equation. This gives that Chitosan bead follow monolayer adsorption of Malachite Green. Chitosan bead showed removal percentage of ninety nine at pH value of eight (optimum). Kinetic experiments shows the process follows pseudo second order knietic model.

In 2010,B.Samiey, AR Toosi conducted studies on the adsorpion of MG on silica gel. The adsorption process obeys Langmuir isotherm for low concentration of Malachite Green. As the MG concentration increases, reverse desorption occurs in MG molecules. The adsorption process happens through chemical bonding.

In 2013, A.S.Sartape, A.M.Mandhare, V.V.Jadhav, P.D.Raut,M.A.Anuse,S.S.Kolekar studied the removal of MG using Mimonia acidissima shell or commonly knows as wood apple shell as adsorbent. The effects of different parameters were investigated and optimal conditions were found out. The Langmuir isotherm fit was found to be more suitable than Freundlich model. The maximum adsorption capacity was found to be 80.645mg/g at 299K

Malachite Green was attempted to be removed from solutions using talc by Y.Lee, M.Choi, J.Yang, H.Shin in 2014. The adsorption kinetics found in the study was found to be following pseudo secong order model. Thermodynamically the adsorption of Malachite Green on talc was found to be endothermic and spontaneous in nature. MG removal using talc was found to be difficult beyond the pH range of 8.0. The percentage removal of talc was found to decline slighly due to the residual malchite green molecules on talc. The most likely reason for this would be that a small fraction of Malachite Green was chemically adsorped on the talc.

Chapter 3

Materials and Methods

3.1 Chemicals and Glasswares

All the reagents used during this work were of analytical grade and distilled water was used to prepare the solution. Chemical used includes Malachite Green Oxalate dye, chemical formula, $C_{16}H_{18}N_3ClS$ and molecular weight of 319.5 was used for the initial adsorption experiments. To vary pH other chemicals such as NaOH and HCl were used. The mentioned chemicals were given by the department laboratory.Glasswares used for the experiments volumetric flasks, pipette, weighing cylinder etc. are all made up of Borosil.All the glasswares were rinsed thoroughly with water several times (tap water) and followed with distilled water.

3.2 Instrumentation

An orbital shaker was used for conducting the adsorption experiments. A UV-ray spectrophotometer was used to find out the absorbance. A muffle furnace was used to semicarbonise the material. A tubular furnace was used to carbonise the material. The pH meter was used to measure the pH of solution. Glass wares were used to handle the solutions. A digital balance was used to weigh the samples.

3.3. Preparation of Adsorbent

The material used to prepare activated carbon i.e. jackfruit seeds were collected from the local market in Station market, Rourkela. The seeds were then washed to remove impurities and crushed into smaller size.

The chemical activation method was employed using phosphoric acid for activating the raw material. 20 gram of raw material was impregnated with 85 wt. % conc. H_3PO_4 and it was stirred. Calculated amount of H_3PO_4 was used to get an impregnation ratio (i.e. weight of the activating agent/weight of the raw material) of 1:1. The slurry formed was then kept inside a desiccator to avoid moisture.

After 24 hours, the slurry was taken out from the desiccator to conduct two-stage activation starting with semi-carbonization. During semi carbonization, the slurry was kept in a crucible to put inside a muffle furnace at 200°C for 30 minutes for experiencing semi carbonization. The slurry of raw material and H_3PO_4 turned black, yielding sticky and black grains. The next stage after semi carbonization it was heated in a tubular furnace at 550°C. The carbonization was performed under the N_2 flow of 100 cm^3/min STP for 45 min. AS the activation gets completed, the activated carbon formed was then collected and finally cooled inside a desiccator to avoid moisture. The formed activated carbon was washed repeatedly with distilled water at 70 °C till the solution reaches constant pH. At last, the washed activated carbon was kept in the oven at 110 °C for 24 h. The resulting activated carbon was kept in the desiccator for further use.

3.4. Adsorbate

The adsorbate is Malachite green dye which is green in colour. It gives bluish-green colored solution in aqueous phase. It is a basic cationic dye and has the molecular formula $C_{52}H_{54}N_4O_{12}$. The molar weight of malachite green dye is 927g, λ_{max} = 615 nm. The aqueous solutions of different concentrations of malachite green dye was prepared by dilution from its originally made solution and the study was done by changing the different parameters.

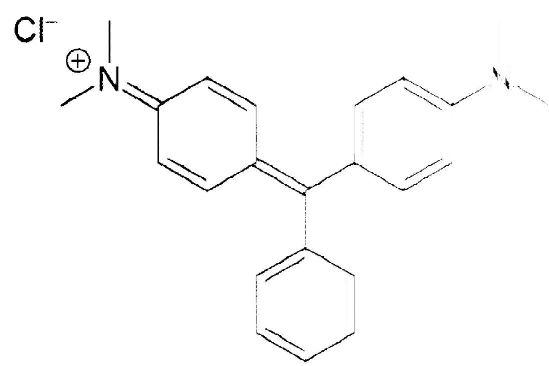


Fig 1. Structure of Malachite green

3.5. Experimental Procedure

The adsorption of malachite green dye using activated carbon prepared from jackfruit seeds was studied using the batch techniques. At first, dye solution of 25ppm was prepared and 1gram of adsorbent i.e. prepared activated carbon was added to it. Another solution with 25ppm concentration of dye was kept. The solution with adsorbent was kept in a shaker for 180 minutes at 115rpm at 30^{o}C under normal conditions. Both the solutions - the one with adsorbent and the one without the adsorbent were analyzed in a UV-vis spectrophotometer. The results obtained from the spectroscopy confirmed that the considerable amount of dye was adsorbed on adding activated carbon. Thus, further studies were feasible. Furthermore, solutions of concentrations varying from 0.78-6.25ppm were prepared and their absorbance was noted through UV spectrophotometer. The results were plotted to get the calibration curve. This curve is the basis for all the future calculations done during this project work.

3.5.1. Study of contact time

A dye solution of 25mg/l was prepared. 1gram of activated carbon was added to it. Then the solution was kept in shaker for 180 minutes at 30^{o}C. Samples were collected at different time intervals. Finally, collected samples and the initial sample which was without adsorbent were analyzed with the spectrophotometer to find out the percent removal of dye and the effect of contact time on it. The % absorbance of UV at 615nm was determined for the samples.

3.5.2. Study of pH

Four working solutions of concentration 25mg/l each were prepared. They were maintained at different pH ranging from 3,5,7,9 by adding dilute HCl or dilute NaOH. Again 1 gram of adsorbent was put in each of 100ml solutions and was kept in orbital shaker at temperature of 30^{o}C with 115 rpm for 1 hour. Samples were collected for each 10 minute interval till 30 minutes and then at 45 and 60 minutes. The collected sample was kept undisturbed for 1 hour and the %absorbance was found with the UV spectrophotometer at 615nm.

3.5.3. Study of adsorbent Dosage

The four solutions of 25mg/l were prepared once again. To each of these solutions, activated carbon in varied amount of 0.5gm, 1gm, 1.5gm and 2gm respectively. These solutions with varied amount of adsorbent dose were then again put into the shaker under the same conditions as used before. The absorbance of each sample was found at 615nm. The results were used to study the effect of adsorbent dosage on the dye removal.

3.5.4. Study of Initial dye concentration

100ml solution of Malachite green solution of concentrations 25ppm, 50ppm, 75ppm and 100ml. To all these solutions, 1gram of activated carbon was added. It was shaken in a shaker at 115rpm and at 30^{o}C. The samples were collected for 1hour and the absorbance was found using the spectrophotometer.

3.5.5 Study of temperature

100ml solutions of concentration 25mg/l were prepared. To all these three solutions, 1gm of adsorbent was added and they were kept for shaking at 120 rpm for 1 hour but at different temperatures of 20^{o}C, 30^{o}C and 40^{o}C. Samples were collected at different intervals and it was analyzed in a UV-spectrophotometer.

Chapter 4

Results and Discussions

4.1. CHARACTERIZATION OF ADSORBATE (Jackfruit seed carbon)

Characteristics	Values
Bulk density (g/cm^3)	0.248
BET surface area (m^2/g)	646.2
Moisture content (%)	2.25%

Table -1 Characterization of Adsorbate

4.2. ADSORPTION STUDIES

Sl No	Concentration	Absorbance
1	6.25	0.956
2	3.125	0.532
3	1.5625	0.266
4	0.78125	0.142

Table:2 The calibration plot for Malachite Green at 615 nm

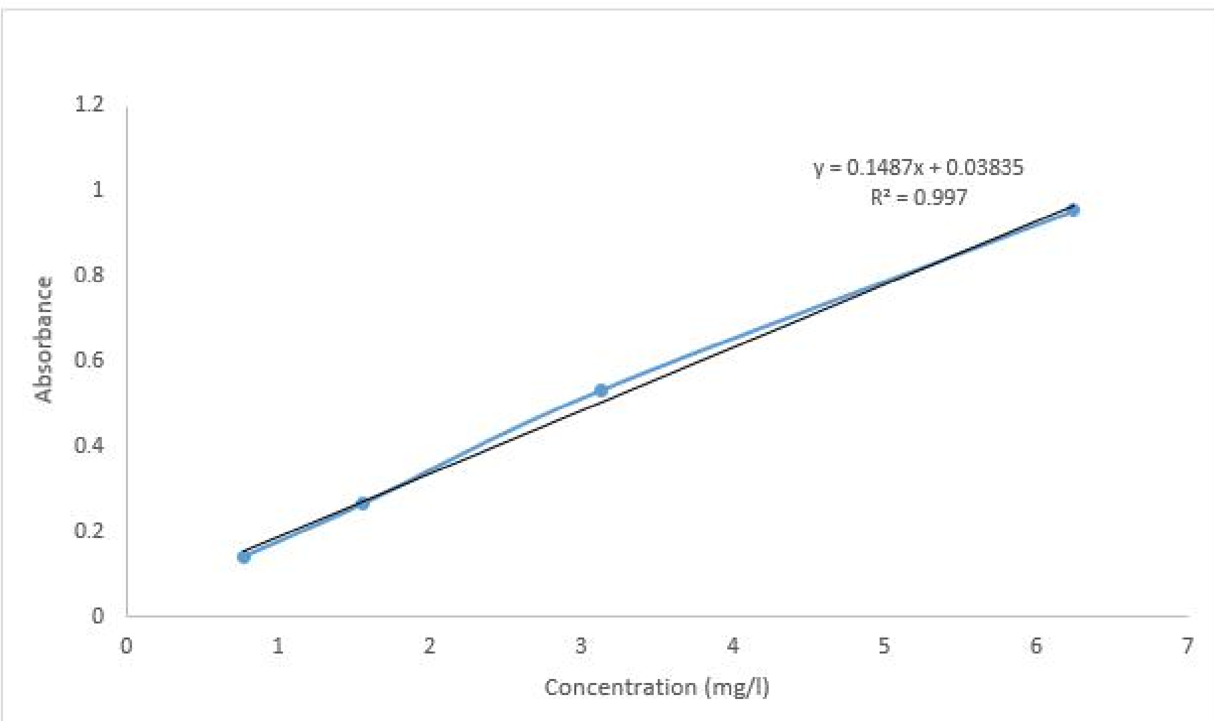


Figure 2. CalibrationPlot

From the graph the slope is found to be 0.1487

Thus, equilibrium concentration at time't', C_e= (absorbance-0.03835)/(0.1327)

4.2.1 Effect of Contact Time

The amount of substance adsorbed per unit weight of adsorbent, qe, was calculated.

q_e= $\{(C_o - C_e)/ w\}*V$,

where C_o = initial concentration of the solution,

Ce = equilibrium concentration at time 't'

W = weight of adsorbent taken

V = Solution Volume

w/V = X , amount of adsorbent per unit volume of solution.

Figure 3 shows the impact of contact time on the adsorption of MG. The rate of adsorption is high initially but it decreases gradually till a point is reached where no significant change can be observed. The concentration of dye does not change significantly after 60 minutes. This shows that the equilibrium time for adsorption as 60 minutes. This happens because of lesser availability of active site and no further adsorption takes place.

This simply can be explained by the fact that initially, the no. of surface sites are very large which allows adsorption to take place very easily. But as the time passes, the active sites get saturated thus slowing down the rate of adsorption.

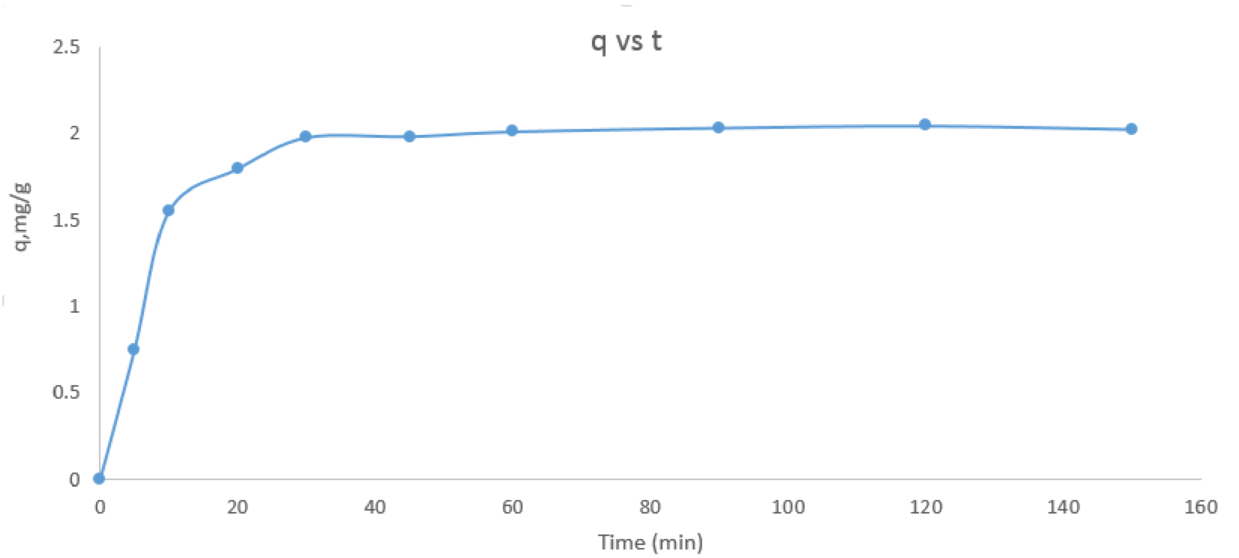


Figure 3. Effect of Contact Time

4.2.2. Effect of Initial pH of the solution

The initial pH of dye solution has a major impact on adsorbent's surface properties and on the degree of ionization of dye molecules. Hence it is important to study the impact of pH on the adsorption process. The figure 4 gives the effect of initial pH on the amount of dye solution adsorbed by activated carbon made from the jackfruit seeds .In the experiment, 100ml of 25mg/L dye solutions in the pH range 3-9 have been studied. The pH of the solutions were adjusted by using 0.1 N HCL and 0.1 N NaOH solution using a pH meter. The results are shown in the figure below and it is clear from the graph that the adsorption capacity of dye is reasonably high in the pH range 3-5 (optimum at 5) and declines at higher ph. At pH 3 there was very small amount of dye removal by jackfruit seed carbon. It can be explained by the fact that for acidic pH, H+ compete with the dye ions for adsorption sites of jackfruit seed carbon, thus inhibiting the adsorption of dye. However at higher pH (>5) ther interaction between malachite green dye and hydroxyl ions occur in its aqueous solution, thus weakening Malachite green color that produces a white precipitate and thus reduced adsorption is reported.

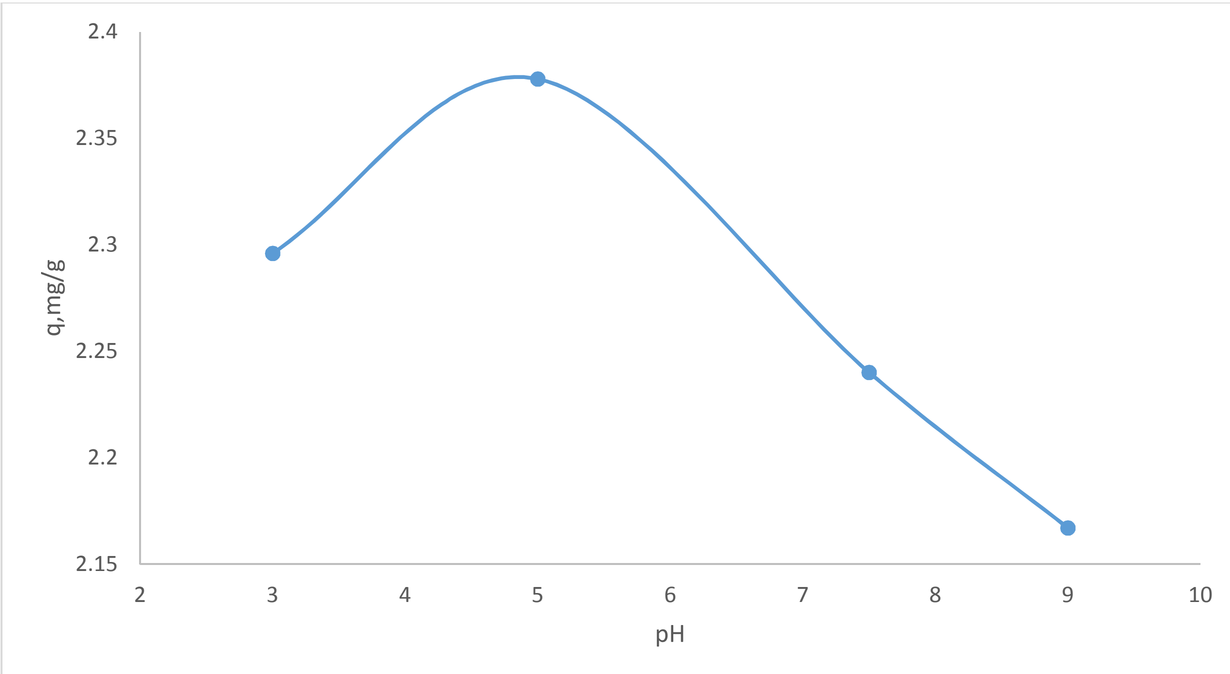


Fig: 4 Effect of solution pH on adsorption of Malachite green dye

4.2.3. Effect of Adsorbent Dosage

The effects of adsorbent i.e. jackfruit seed carbon dose on the percentage removal of dye at initial concentration of 25mg/l at room temperature was studied for different dosage of 0.5g,1.5g and 2g in 100ml solution. Figure 5 shows that the adsorption capacity decreases with increase in the adsorbent. The percentage removal increases with the increase in dosage. This can be explained by the fact that on increasing adsorbent dosage, the surface area of the adsorption sites increases. But there is no significant increase in adsorption capacity further even after adding more adsorbent which might be due to the interactions between particles within themselves.

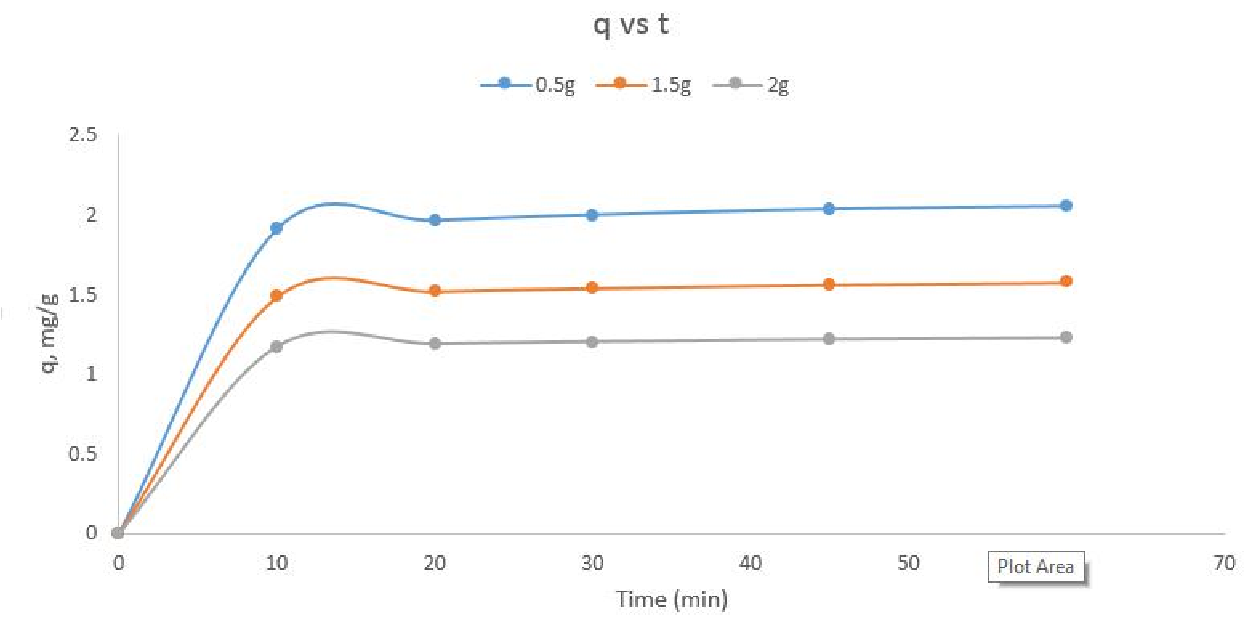


Fig: 5 Effect of adsorbent dose on the adsorption of Malachite green dye

4.2.4. Effect of Initial Dye Concentration

The concentration of dye has an apparent influence on its removal from aqueous phase. The effect of malachite green dye conc. on the efficiency of adsorption was also investigated in the initial concentration range of 50-100 mg/L. The adsorption capacity at equilibrium increases with increase in initial dye concentration. This trend could be attributed to the fact that at high concentration of dye, driving force is high for mass transfer. If the dye concentration is higher on the solution, active sites of the adsorbent are surrounded by higher number of dye molecules which leads to more efficient adsorption.

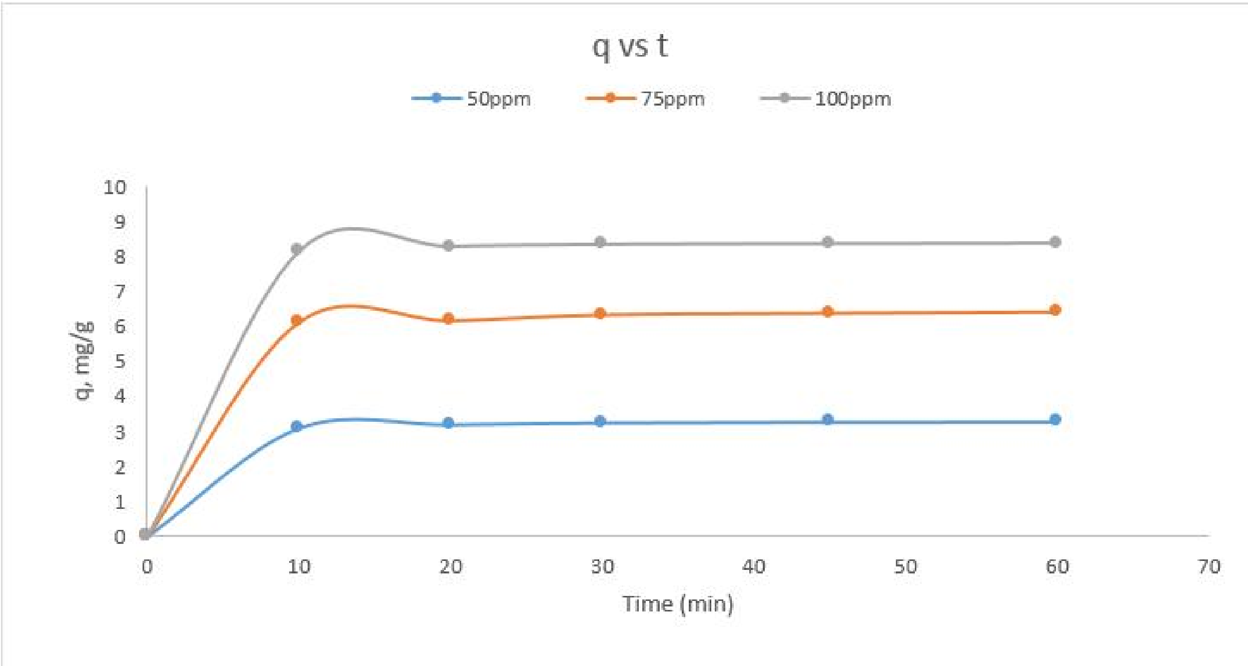


Fig: 6 Effect of initial concentration of Dye solution

4.2.5. Effect of Temperature

Temperature is also a notable controlling factor in the real applications of adsorbent for the dye removal process. Figure represents the adsorption of malachite green by jackfruit seeds at different temperatures of 20, 30 and 40^{o}C. The temperature affects the dye adsorption efficiency positively which means that the removal percentage of dye increases with the increase in temperature of the system from 20 to 30 ^{0}C. This trend is attributed to the fact that chemical interactions takes place between the malachite green dye and adsorbent which is endothermic in nature. However beyond 30 ^{0}C the percentage dye removal reduced.

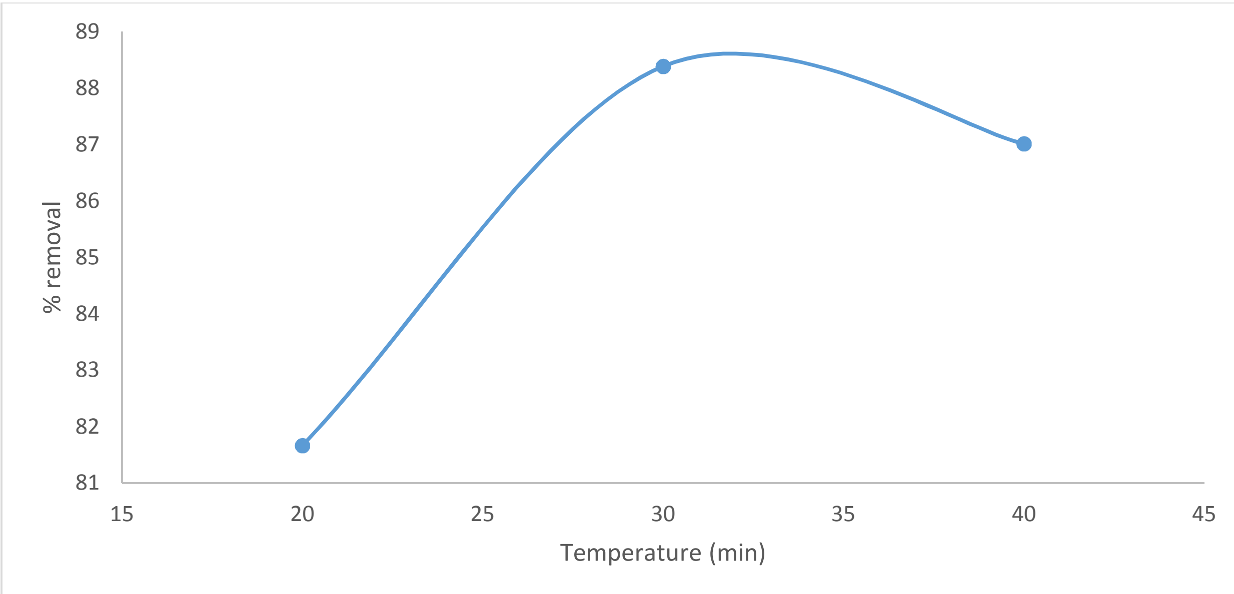


Fig : 7 Effect of Temperature on dye removal

4.3. Adsoprtion Isotherm Studies

4.3.1 Langmuir Isotherms

It gives the relation between the adsorption of the molecules on solid surface to the gas pressure or conc. of a medium above surface of solid at constant temperature. It is based upon the assumption that adsorption process occurs in monolayers.

The linear form of Langmuir expression:

$$\frac{1}{q_e} = \frac{1}{b * q_0 * C_e} + \frac{1}{q_0}$$

Where, C_e = equilibrium conc. of dye solution (in mg/L),

q_e = equilibrium capacity of the dye on adsorbent (in mg/g),

q_o = monolayer adsorption capacity of adsorbent (in mg /g),

b = Langmuir adsorption constant (in L/mg) and has realtion with the free energy of adsorption.

The value of Langmuir constants q_o and b from the linearized form of the Langmuir isotherm Equation was calculated by plotting graph between 1/qe vs 1/Ce. The correlation coefficients (R^2) are not satisfactory, so the adsorption does not follow the Langmuir model.

Temperature	q_o	b	R^2
30°C	7.5415	0.370	0.9262

Table: 3 Langmuir isotherm constants

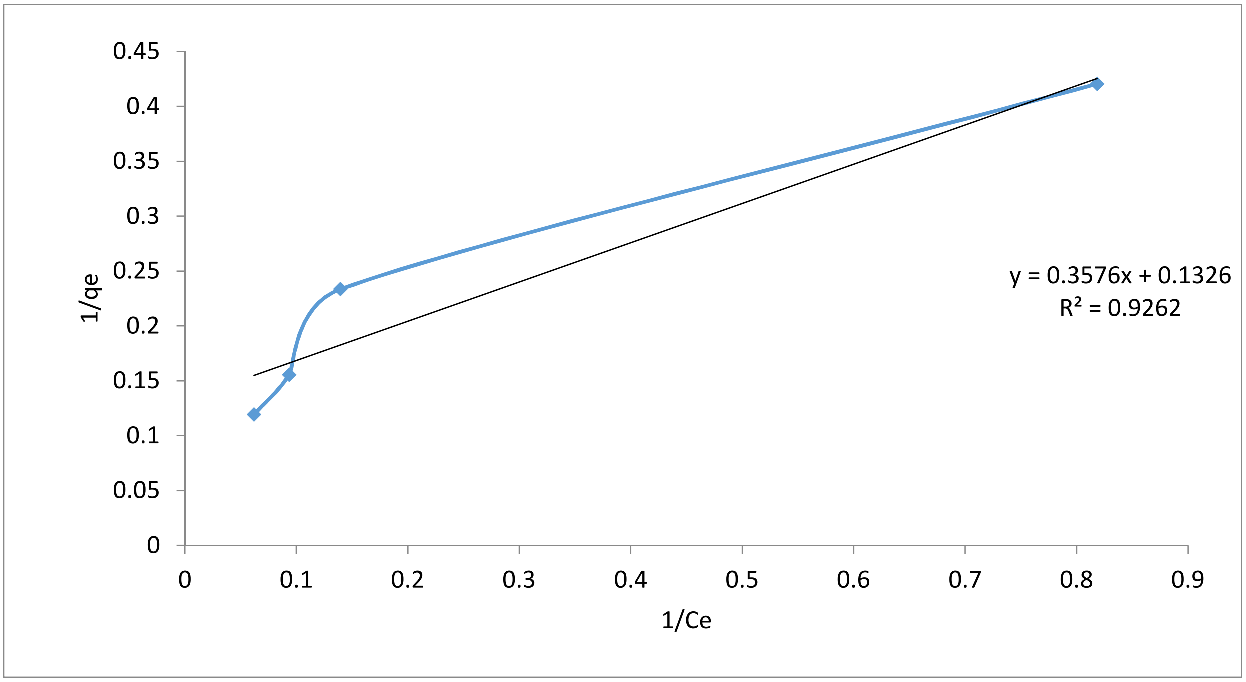


Figure 8: Langmuir isotherm plot for adsorption of MG by ACs prepared from jackfruit seeds

4.3.2 Freundlich isotherm

It is an empirical relationship which relates the conc. of a solute upon the surface of the adsorbent with the conc. of solute present in the liquid which are in contact. This model assumes that adsorption occurs on heterogeneous surface.

The linear form can be written as:

$$\ln q_e = lnk_f + \frac{1}{n * lnC_e}$$

Where, k_f and n (dimensionless constants) are Freundlich adsorption isotherm constants.
k_f gives adsorption capacity and n gives the adsorption intensity. The values of k_f and n were found from the linearized form of Freundlich isotherm equation which was done by plotting graph between ln q_e vs. ln C_e.

Temperature	K_f	n	R^2
30°C	2.0507	2.13	0.9448

Table: 4 Freundlich isotherm constants

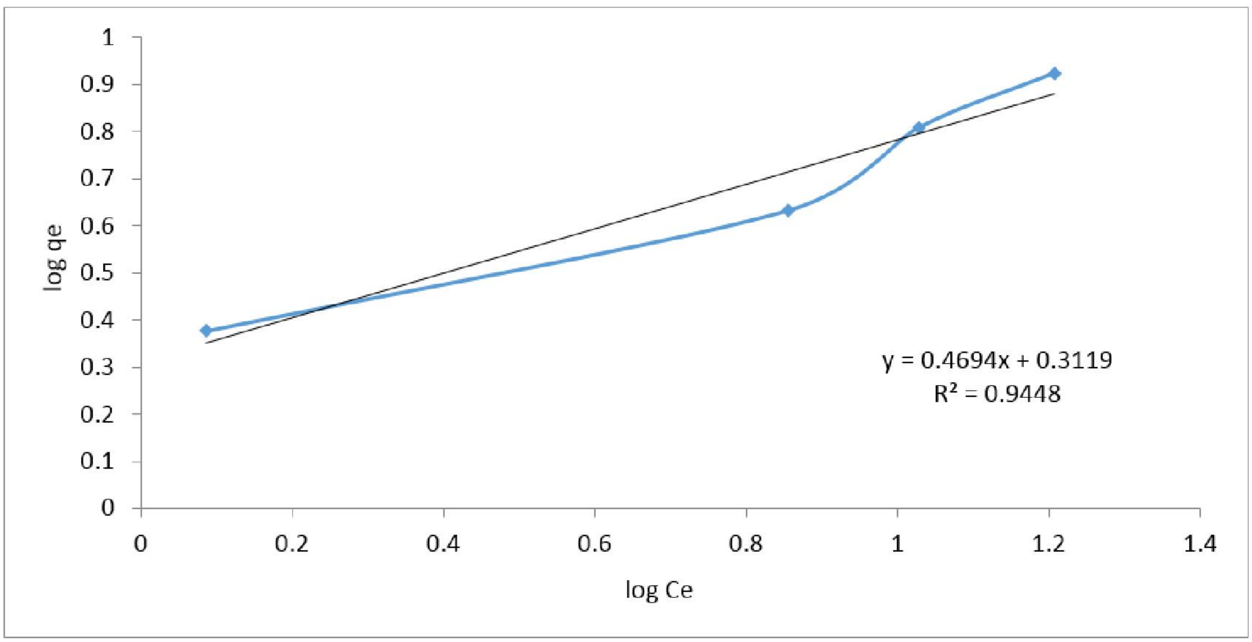


Figure 9: Freundlich isotherm plot for the adsorption of MG by AC prepared from jackfruit seeds

The R^2 values of Freundlich isotherm shows that it is more suitable than the Langmuir isotherm.

Chapter 5
Conclusion

The following observations were made after conducting the experiments and doing the calculations:-

- Adsorption increases with the increase in the contact time. At first the rate of adsorption is very high which is due to free sites available for adsorption. Rate of adsorption decreases till the equilibrium is reached. The equilibrium contact time was found to be one hour.
- The removal efficiency of the activated carbon is maximum at pH 5 and it declines when the pH of the initial solution is increased further.
- Adsorption increases with the increase in the adsorbent dose due to the availability of free sites.1g/100ml concentration of adsorbent is taken as the optimum adsorbate dose. As the adsorption capacity is higher for 1gm of adsorbent.
- There is increase in adsorption with the increase in initial dye concentrations. This is due to the fact that with higher initial dye concentration the driving force for mass transfer also gets higher.
- Adsorption capacity is found to be optimum at 30^{o}C, which has been used throughout the studies.
- The Freundlich isotherm is more suited than the Langmuir isotherm.

Thus it can be concluded that jackfruit seeds, which are in abundance in the country, can be used for the removal of malachite green dye from waste water. Further, there is scope of more study and research which can enhance the removal percentage of malachite green and also, the feasibility of jackfruit seeds for removal of other dyes.

Chapter 7

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